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Article

The Effects of Some Phosphorus-Containing Fire Retardants on the Properties of Glass Fibre-Reinforced Composite Laminates Made from Blends of Unsaturated Polyester and Phenolic Resins

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Abstract: This study investigated the effects of phosphorus fire retardants (FRs) in matrices from co-cured blends of an unsaturated polyester (UP) with inherently fire-retardant phenolic resoles (PH) on the mechanical and flammability properties of resultant glass fibre-reinforced composites. Three different phenolic resoles with UP have been used: (i) an ethanol soluble (PH-S), (ii) an epoxy-functionalised (PH-Ep), and (iii) an allyl-functionalised resin (PH-Al) with two different phosphorus FRs: resorcinol bis (diphenyl phosphate) (RDP) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). The flammabilities of the resultant composites were evaluated using cone calorimetry and the UL-94 test. Cone calorimetric results showed reductions in peak heat release rate (PHRR) and total heat released (THR) as expected compared to those of UP and respective UP/PH composite laminates without FRs. UL-94 tests results showed that while all composites had HB rating, FR containing samples self-extinguished after removal of the flame. The mechanical properties of the composites were evaluated using flexural, tensile and impact tests. All FRs reduced the mechanical properties, and the reduction in mechanical properties was more severe in UP/PH-S (least compatible blends) composites with FRs than in UP/PH-Al (most compatible blends) composites with FRs. Amongst the different composites, those from UP/PH-Al with DOPO showed the best fire retardancy with little deterioration of mechanical performance.

Keywords: phosphorus-based fire retardants (FRs); glass fibre-reinforced composite (GFRC); blends; unsaturated polyester; phenolic resoles; mechanical properties; fire properties



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1. Introduction

Unsaturated polyester (UP) based glass fibre-reinforced composite (GFRC) is one of the widely used composites in marine applications owing to its excellent mechanical properties, good moisture resistance, and good corrosion and chemical resistance [1–5]. Despite these advantages, poor fire resistance, the evolution of smoke and emission of styrene during burning are the major limiting factors for applications of UP based composites where fire safety is important such as in passenger vessels, naval ships, submarines, etc. [1,2]. In order to meet the stringent marine fire safety regulations governed by the authorities such as IMO/HSC (International Maritime Organization/Code of Safety for High Speed Craft), glass fibre-reinforced composites (GFRC) of UP need to be rendered fire retardant [6,7].

The intrinsic flammability of UP can be altered either by chemical modification of the resin or by adding fire retardant chemicals into it [8,9]. Each method has drawbacks associated with it such as the following: the chemical modification of UP usually involves using halogenated elements, which raises environmental issues [10]; high concentrations (typically >30 wt.%) of mineral fillers such as aluminium trihydrate and magnesium hydroxide

or inorganic phosphates cause deleterious effects upon physical and mechanical properties and processing difficulties [11,12]. An alternative approach is to use protective surface coatings of ceramic or intumescent materials, but these cause additional weight [13–15]. A different approach to improve the fire retardancy of cured UP is clearly required and, with this in mind, UP can be blended with other polymers and co-cured to give materials fire retardancy better than that of cured UP alone. Polymer blending is a well-established, convenient and inexpensive technique involving physical mixing of at least two polymers to accentuate or suppress specific properties of the individual polymers in the resultant blend [16]. For example, phenolic (PH) resin with excellent fire retardance, good heat resistance, low smoke and toxic gas evolution can be blended with UP resin to improve the poor fire resistance of UP [17–20]. While PH resins generally have excellent fire retardance, they are brittle and have poor mechanical properties [20]. UP on the other hand has excellent mechanical properties. Hence, the resultant UP/PH blends are expected to have optimal fire and mechanical properties [17–20]. Blending of resins by physical means such as mechanical stirring with a high shear force will lead to the formation of either interpenetrating networks (IPNs) or hybrid polymer networks (HPNs) without any chemically active covalent bonds [21,22]. A resultant property of a resin blend mainly depends on the chemical miscibility of the blended materials and the processing conditions [23]. Although some examples of these are given in literature, this is not a common method for fire retarding composites. Based on the work carried out previously in the University of Bolton's Fire Materials Group, it was envisaged that blending can produce resins with inherently fire-retardant properties [24–27]. UP resin was blended with three different commercially available resoles comprising (i) containing a compatibilising solvent, ethanol (PH-S), and chemically modified to contain (ii) hydrophobic and reactive epoxy groups (PH-Ep) and (iii) free-radically reactive allyl groups (PH-Al). The compatibility behaviour, fire performances and the mechanical properties of different UP/PH blended systems were studied. The results indicated that there is evidence of increasing compatibility (PH-Al > PH-Ep > PH-S) of these phenolic resins with UP which had been supported with differential scanning calorimetry (DSC), differential mechanical thermal analysis (DMTA), solid state ^{13}C -NMR and scanning electron microscopy (SEM) studies in our previous work [25,26]. Glass transition temperatures (T_g) of UP/PH-S showed two T_g values and UP/PH-Ep with a less well-defined second one in the latter and only a single T_g in the most compatible system (UP/PH-Al) [25,28]. The least compatible blended resin of UP/PH-S had, however, shown the best fire retardancy but with the poorest mechanical properties [28,29], whereas compatible resin blends of UP with functionalised resoles (PH-Ep and PH-Al), which had better physical and mechanical properties, were less fire retardant. In order to improve the fire retardancy of the latter, selected liquid/reactive fire retardants (FRs) were added to the resin blends [27]. The FRs chosen were resorcinol bis (diphenyl phosphate) (RDP), bisphenol-A bisdiphenyl phosphate (BADP) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). RDP and BADP were added at 20 wt.%, while DOPO was used at 10 wt.% [27]. The fire-retardant action of these FRs additives involves both gas-phase and condensed-phase components as indicated by increased yields of both smoke and char on combustion. The FRs were, however, least effective in the least compatible co-cured UP/PH-S blends.

While in the previous work, discussed above, it was established that certain FRs can be successfully added to the UP/PH blends without a detrimental effect on the curing behaviours, their effects on the processability during GFRC preparation and on the fire and mechanical properties of the resultant structural composites are not known, which is the focus of this study. Here GFRCs from UP/PH blends with 70/30 wt.% ratios containing RDP (20 wt.%) and DOPO (10 wt.%) have been prepared, and their mechanical and fire performances evaluated. The UP/PH 70/30 wt.% ratio was selected based on the optimum fire retardant and mechanical properties seen for this blend in the previous study [29].

2. Materials and Methods

2.1. Materials

Unsaturated polyester (UP): Crystic[®] 2-406PA (Scott Bader, Wellingborough, UK), a phthalic anhydride-based and pre-accelerated with cobalt octoate.

Catalyst M (Scott Bader): methyl ethyl ketone peroxide dissolved in methyl ethyl ketone.

Solvent based phenolic (PH-S): Durez 33156 (Sumitomo-Bakelite Europe N.V., Genk, Belgium), an ethanol-based phenolic resole containing 20–29 wt.% ethanol.

Epoxy functionalised phenolic (PH-Ep): Plyophen 23983 (Sumitomo-Bakelite Europe N.V.), an isopropanol-based, epoxy-functionalised, phenolic resole containing 16–18 wt.% isopropanol and <6 wt.% water.

Allyl functionalised phenolic (PH-Al): Methylon 75108 (Sumitomo-Bakelite Europe N.V.), a solvent-free, allyl-functionalised, phenolic resole.

Resorcinol bis(diphenyl phosphate) (RDP), Chemtura UK.

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), Tokyo Chemical Industry UK Ltd., Oxford, UK.

Woven roving E-glass fibre, 300 gm/m² (Glasplies, Southport, UK).

2.2. Composite Preparation

Blends of UP/PH with 70/30 wt.% ratios were prepared by mixing required quantities of UP and PH. RDP and DOPO were added in 20 wt.% and 10 wt.% of total resin content with mechanical stirring and then degassed under vacuum for 15 min. A methyl ethyl ketone peroxide catalyst (2 wt.% w.r.t. resin) was added into the resin mixture and stirred for another 10 min.

Eight layers of E-glass fabric of size 300 mm × 300 mm were used for GFRC preparation by wet hand lay-up method, keeping the glass fabric and resin ratio 50/50 wt.%. Each layer of fabric was impregnated with UP or UP/PH resin with and without FR, stacked, vacuum bagged and cured using curing conditions listed in Table 1. The composites from pure resole phenolic resins could not be prepared because of their low viscosities at high temperatures which led to too much of leak-out when curing.

Table 1. Composition of the GFRC from UP and UP/PH blends with FRs.

Sample ID	Thick (mm)	Fibre (wt.%)	Resin (wt.%)	FVF (%)	Curing Conditions
UP	2.4	59	41	39	RT 24 h, 80 °C 6 h
UP/PH-S:70/30	2.5	59	41	38	50 °C 6 h, 80 °C 24 h, 90 °C 9 h, 130 °C 1 h, 160 °C 1 h
UP/PH-S:70/30-R	2.2	66	34	34	50 °C 6 h, 80 °C 24 h, 90 °C 9 h, 130 °C 1 h, 160 °C 1 h
UP/PH-S:70/30-D	2.4	59	41	41	50 °C 6 h, 80 °C 12 h, 90 °C 8 h, 110 °C 6 h, 130 °C 6 h, 150 °C 2 h, 180 °C 2 h
UP/PH-Ep:70/30	2.6	59	41	38	50 °C 6 h, 70 °C 8 h, 80 °C 8 h, 100 °C 6 h, 130 °C 2 h, 160 °C 2 h
UP/PH-Ep:70/30-R	2.1	64	36	36	50 °C 6 h, 70 °C 8 h, 80 °C 8 h, 100 °C 6 h, 130 °C 2 h, 160 °C 2 h
UP/PH-Ep:70/30-D	2.8	55	45	45	50 °C 6 h, 70 °C 12 h, 90 °C 8 h, 110 °C 6 h, 130 °C 6 h, 150 °C 2 h, 180 °C 2 h
UP/PH-Al:70/30	2.4	59	41	38	50 °C 6 h, 80 °C 12 h, 100 °C 8 h, 120 °C 6 h, 130 °C 6 h, 150 °C 2 h, 180 °C 2 h
UP/PH-Al:70/30-R	2.2	63	37	37	50 °C 6 h, 80 °C 12 h, 100 °C 8 h, 120 °C 6 h, 130 °C 6 h, 150 °C 2 h, 180 °C 2 h
UP/PH-Al:70/30-D	2.6	54	46	46	50 °C 6 h, 80 °C 12 h, 100 °C 8 h, 120 °C 6 h, 130 °C 6 h, 150 °C 2 h, 180 °C 2 h

Note: Thick = thickness, FVF = fibre volume fraction; R = RDP and D = DOPO.

2.3. Fire Testing

The flammability and the fire performance of GFRFC composite laminates samples were evaluated by a cone calorimeter (Fire Testing Technology, East Grinstead, UK) in accordance with ISO 5660 [30], except that the sample size used was 75 mm × 75 mm × ~2.1–2.8 (Table 1). Smaller than usual samples were used here in order to allow comparisons with the results of previously reported experiments [29] carried out on similarly small samples. Moreover, reported results for composites in this paper are discussed in comparative terms with respect to control UP; hence, the use of 75 mm square plaques may not be that important in terms of compliance to ISO 5660 standard. Before testing, the bottom surface and the edges of the samples were wrapped with aluminium foil to ensure that only the top surface would be directly exposed to the heat source. A minimum of three tests were performed for each formulation by exposing them to 50 kW/m² incident heat flux in the horizontal mode with an ignition source.

A standard method UL-94 (ISO 1210), using an UL-94 apparatus as specified by the Underwriters Laboratories, was also used to evaluate the fire performances of the GFRFC samples. In the vertical UL-94 testing mode, specimens were exposed to a flame (20 mm height) generated from a methane gas burner with a gas flow rate of 105 mL/min for 10 s. Following the withdrawal of the flame, the time taken before the specimen self-extinguishes, t_1 , was recorded. The specimen was re-ignited, and the burning time, t_2 , was recorded. Average results of three tests for each sample are reported. The flaming drips from the sample were evaluated by the cotton fibres positioned 300 mm below the test specimen.

The samples are classified on the basis of standard criteria conditions. If the sample self-extinguishes within 10 s after each ignition and no dripping is observed, the sample is classified as V-0. If it self-extinguishes within 30 s with no flaming drips then the sample is classified as V-1; however, if flaming drips ignite the underlying cotton, it is classified as V-2. If the sample burns completely, it is classified as “fail”.

In the horizontal test, the sample was supported horizontally, and its free end was subjected to a calibrated flame of 20 mm height for 30 s. The sample was marked off at 25 mm and 100 mm from its exposed end, to enable measurement of the burning length. After the flame passes the 25 mm mark, the time was recorded until the flame reaches the 100 mm mark, from which rate of burning was calculated as

$$V = \frac{L \times 60}{t} \quad (1)$$

where V is the burning rate in mm/min; L is the length of the sample in mm, and t is the time of burning for the middle 75 mm of the sample in seconds. Two replicate specimens of each sample were burnt and results averaged. The burning behaviour of each sample was observed and noted.

2.4. Mechanical Property Measurements

The flexural testing of the GFRFC laminate samples (150 mm × 20 mm × thickness as in Table 1) was measured according to BS EN ISO14125 [31] in three-point bending mode using a Universal Instron 3369 tensiometer. A 100 N load cell with the compression rate 1 mm/min was used on the samples with the span length of 100 mm. Tests were undertaken within the elastic region of the samples. On one of the specimens of each sample, a strain gauge was attached to accurately measure the strain and displacement. The flexural modulus (E) of the samples was calculated using the three-point bending Equation (2) [32],

$$E = \frac{FL^3}{4sbh^3} \quad (2)$$

where F is the applied load, and s is the displacement; L is the span length; b and h are the width and thickness of samples, respectively. Results reported are averages of three replicate tests.

Tensile testing was carried out according to BS EN ISO 527 using an Instron 3369 universal testing machine. The gauge length of each specimen (150 mm × 20 mm × thickness as in Table 1) was 100 mm and polymeric tabs were bonded at their ends to improve the gripping and ensure failure within the gauge region. The tests were conducted using a 50 kN load cell with a crosshead speed of 1 mm/min. Tensile modulus and strength values were calculated from stress–strain curves using an extensometer. Selected samples had strain gauges bonded to their surfaces to verify the results. Results reported are an average of three replicate specimens.

The impact properties of the GRFC laminate specimens were measured using an Instron Dynatup instrument in accordance with ASTM D7136. The samples, sized 75 mm × 75 mm × thickness as in Table 1, were fully clamped on the sample holder, which has a hole (76.2 mm diameter) in the centre. The clamped samples were impacted by dropping a steel impactor of 16 mm crosshead diameter and 1.02 kg drop mass from 100 mm height with an impact velocity of 1.38 m/s to produce the impact energy of 1.0 J on the sample. A high-speed data acquisition system (Dynatup® Impulse™ software data capture system) was used to obtain load–central displacement curves. The impact modulus of each sample was calculated using the following Equation (3) [33],

$$\text{Impact modulus } E_i = \frac{3D}{4\pi t^3}(K) \quad (3)$$

where D is the diameter of the hole of the sample holder; t is the thickness, and K is the stiffness. Three replicate specimens of each sample were tested, and the results averaged. From the digital images of the tested sample, the damaged area was measured and compared with that of the control sample.

3. Results and Discussion

3.1. Fire Performance of Glass Fibre-Reinforced UP/PH Blended Composites

3.1.1. Cone Calorimetry

The heat release rate (HRR) vs. time curves and rate of smoke release (RSR) vs. time curves for GFRC laminate systems of UP, UP/PH-S, UP/PH-Ep and UP/PH-Al with and without FRs are shown in Figure 1a–c, respectively. The derived parameters are listed in Table 2. Since the resin contents in all samples were slightly different, selected cone parameters (CP) were normalised w.r.t. 40 wt.% resin contents as

$$CP_{\text{Normalised}} = \frac{CP_{\text{Absolute}}}{\text{Resin wt.\%}} \times 40 \quad (4)$$

The normalised (N) values are also given in parentheses after the actual values in Table 2. In Figure 2, the % reduction of each cone parameter w.r.t. for UP (normalised values, N) is given.

The cone calorimetric results of GFRCs of UP, UP/PH-S, UP/PH-Ep and UP/PH-Al have been discussed in detail in our previous publication [29] and summarized here. The GFRC of UP ignited at 38 s (represented by time-to-ignition (TTI) in Table 2) and burned for 146 s (FO time, Table 2), producing 491 kW/m² peak heat release rate (PHRR) and 32.6 MJ/m² total heat release (THR). For co-blended UP/PH-S and UP/PH-Ep composite samples, TTI is little affected by the presence of the phenolic resin, the values being similar to, or slightly less, than that of the UP composite. However, TTI of GFRC from co-blended compatible resin, UP/PH-Al, is higher than those of all composite samples, including the control UP. This may be due to the UP/PH-Al blend being co-cross-linked [25,26] and hence displaying the ignition behaviour of a homogeneous material, whereas in UP/PH-S and UP/PH-Ep composites, the two resins are not intimately cross-linked and exist as two separate phases. In Figure 1, all co-blended (UP/PH-S, UP/PH-Ep and UP/PH-Al) composite samples show single peaked HRR-curves, similar to that of the UP composite sample, but the intensity of each peak is lower, representing a lower peak heat release rate. PHRR and THR are reduced in all composites from co-blended samples compared to the

control UP sample, but as can be seen in Figure 2, the reduction is more in UP/PH-S than others, being least in UP/PH-Al.

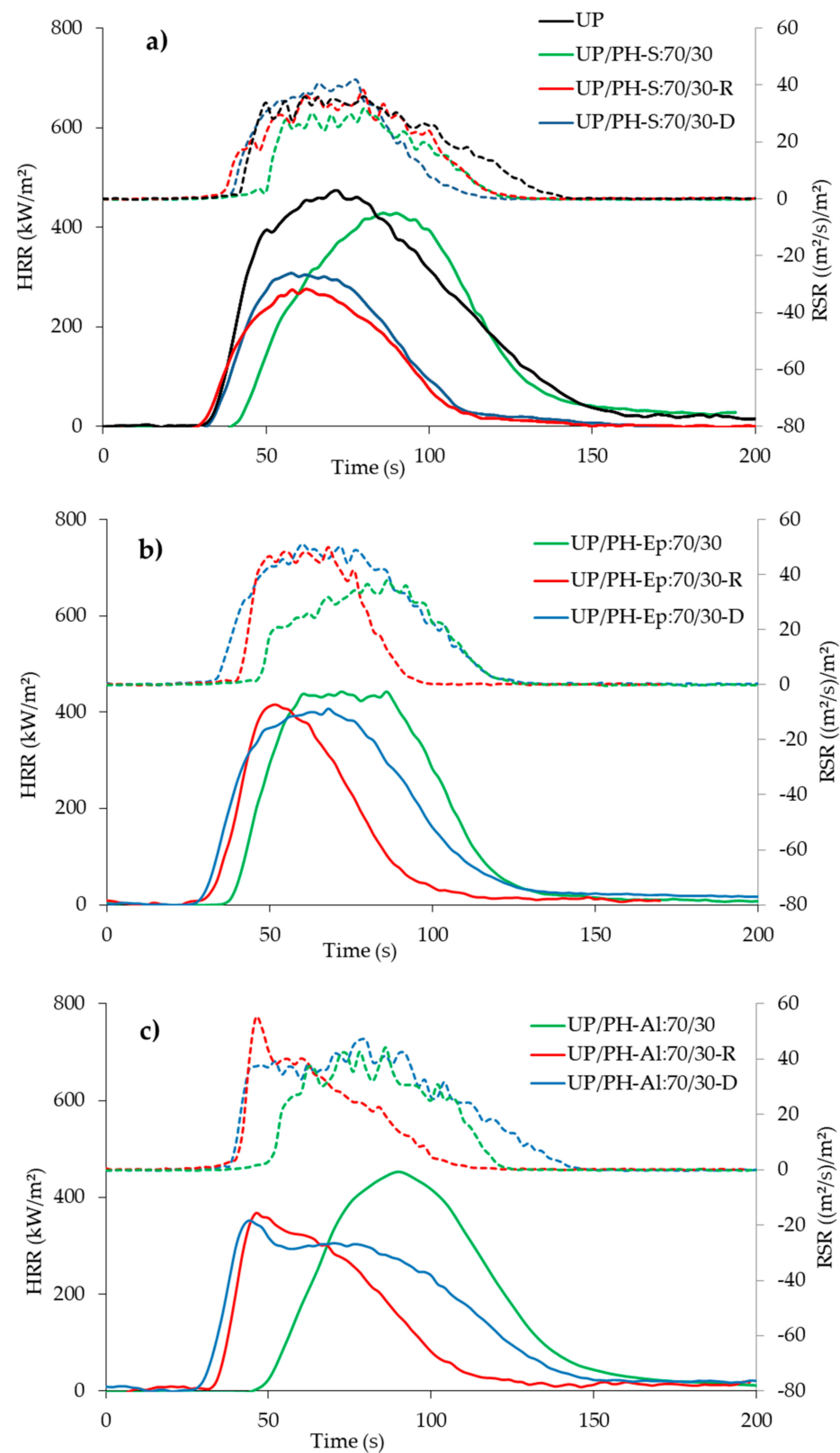


Figure 1. (a–c) HRR vs. Time (solid lines) and RSR vs. Time (broken lines) curves of UP/PH-S, UP/PH-Ep and UP/PH-Al GFRC samples at 50 kW/m² heat flux.

Table 2. Cone results for GFRC of UP and UP/PH blends with and without FRs exposed to 50 kW/m² heat flux.

Sample	Resin wt. (%)	TTI (s)	FO (s)	PHRR (kW/m ²)	THR (MJ/m ²)	TSR (m ² /m ²)	Res. mass (%)	FIGRA (kW/m ² s)
UP	41	38	146	491(479)	32.6 (30.3)	2233 (2077)	59.8 (58.3)	9.1 (8.9)
UP/PH-S:70/30	41	39	140	428 (418)	26.9 (26.2)	1482 (1446)	64.0 (62.4)	5.6 (5.5)
UP/PH-S:70/30-R	34	36	129	287 (338)	14.6 (17.2)	1888 (2221)	67.2 (79.1)	4.6 (5.4)
UP/PH-S:70/30-D	41	37	142	345 (337)	18.4 (14.2)	1900 (1853)	63.2 (61.7)	4.9 (4.8)
UP/PH-Ep:70/30	41	42	132	415 (461)	25.9 (25.3)	1689 (1648)	62.0 (60.5)	6.4 (6.2)
UP/PH-Ep:70/30-R	36	37	111	402 (447)	14.3 (15.9)	1726 (1918)	70.2 (78)	6.1 (6.8)
UP/PH-Ep:70/30-D	45	36	136	408 (363)	23.4 (20.8)	2616 (2325)	61.5 (54.7)	6.0 (5.4)
UP/PH-Al:70/30	41	46	131	454 (443)	29.4 (28.7)	1769 (1726)	56.9 (55.5)	6.9 (6.7)
UP/PH-Al:70/30-R	37	38	128	368 (398)	17.4 (18.8)	1823 (1971)	68.1 (73.6)	5.1 (5.5)
UP/PH-Al:70/30-D	46	35	166	352 (306)	24.2 (21.0)	2919 (2538)	61.8 (53.7)	4.5 (3.9)

Note: The variation in values for different parameters are the following: TTI = ± 3 ; FO = ± 6 ; PHRR = ± 26 ; THR = ± 1.2 ; TSR = ± 104 ; Res. mass = ± 1.6 ; FIGRA = ± 0.8 . The values within parentheses are the normalised (N) values with respect to the 40% (wt.) resin.

**Figure 2.** Percent changes in cone parameters and flexural/tensile/moduli of GFRC from (a1,a2) UP/PH resins, (b1,b2) UP/PH containing RDP and (c1,c2) UP/PH containing DOPO w.r.t control GFRC of UP.

The smoke production is also reduced in all UP/PH resins. The control sample, UP burned completely, leaving no residue. In all co-blended resins, there was some residue left, as can be seen in Figure 3, where some residue can be observed within the layers of glass fabrics of the cone burnt samples, also seen in Figure 2 as a residual mass increase in these samples compared to UP, indicating the charring tendency of phenolic resins.

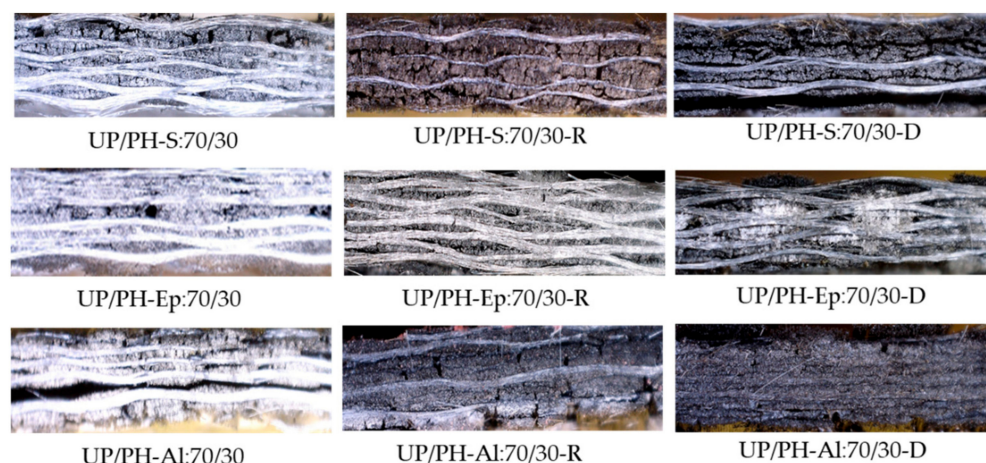


Figure 3. Digital microscopic images of GFRC samples after cone experiments.

As can be seen in Figure 1 and Table 2, the GFRCs of co-blended samples containing RDP (R) or DOPO (D) fire retardants (FRs) have lower TTI than the respective blends without FRs, which can be explained due to the lower decomposition temperatures ($<250^{\circ}\text{C}$) of these FRs than those of the UP and PH resins [27]. The presence of P-O bonds in RDP and DOPO is less stable than the common C-C, C-H and C-O bonds in UP [34–36]. The earlier ignition of GFRC samples of UP/PH-Ep and UP/PH-Al and resins containing FRs is attributed to the accelerated decomposition of the FR in the resin matrix and is consistent with the observation from previously reported TGA results [27] that the decomposition temperatures of the FRs are lower than those of the PH-Ep and PH-Al resins.

The GFRCs of UP/PH-S:70/30-R and UP/PH-S:70/30-D samples show reduced peak heat release rates (PHRR) of 287 (338 N) kW/m^2 and 345 (337 N) kW/m^2 , respectively, which is a 30% decrease (Table 2 and Figure 2(a1)) with respect to PHRR of UP composite and 19% decrease with respect to UP/PH-S:70/30 (Table 2). From the shapes of HRR curves of UP/PH-S:70/30 composites containing FRs, it can be seen that the burning processes are of shorter duration than those of UP and UP/PH-S:70/30 (see Figure 1a) which indicates the reduced flammability of composites containing FRs. The composites of UP/PH-S:70/30 with FRs have lower PHRR and THR than those of UP/PH-S:70/30 (see Table 2) whereas the amount of charred residue and the total smoke released (TSR) has increased (Figure 2(a1)). The TSR of UP/PH-S:70/30-R and UP/PH-S:70/30-D composites are higher than those of UP and UP/PH-S:70/30 composites, respectively. This higher smoke emission and lower char yield indicate that the RDP and DOPO are acting mainly in the gas phase [27]. The higher char yield was also seen in TGA results of the cast resins reported previously [27]. In RDP and DOPO, a volatile phosphorus containing oxidation product from the thermolysis of the FR acts as a free radical chain stopper in the gas phase mechanism. The $\bullet\text{PO}$ radical, which is produced readily from RDP and DOPO by a radical transfer reaction is responsible for the improved fire retardancy of the co-blended composites with FRs; this mechanism has been discussed in detail elsewhere [27]. From the cone results for the GFRC of UP/PH-S matrix, with and without FRs, the order of fire retardancy based on the PHRR and THR is

$$\text{UP/PH-S:70/30-D} > \text{UP/PH-S:70/30-R} > \text{UP/PH-S:70/30} > \text{UP}$$

From Figure 1b and Table 2, it can be seen that the GFRC of UP/PH-Ep:70/30-R and UP/PH-Ep:70/30-D show lower flammability with reduced PHRR (402 (447 N) kW/m^2

and 408 (363 N) kW/m²) and THR (14.3 (15.9 N) MJ/m², 23.4 (20.8 N) MJ/m²) compared with those of UP and UP/PH-Ep:70/30 composite cone parameters. The % changes in values with respect to those of UP GFRC are plotted in Figure 2. From Figure 2 and Table 2, the % char yields of UP/PH-Ep GFRCs containing RDP and DOPO are 6.2% and 6.5%, respectively, i.e., higher than those of UP and UP/PH-Ep:70/30. The higher smoke emission and higher char yields indicate that FRs are acting both in gas phase and condensed phase in the UP/PH-Ep co-blended resin composites [27,29]. In UP/PH-Ep:70/30 GFRCs with DOPO, there is the additional possibility that the epoxy groups in PH react with the P–H bonds of DOPO in a nucleophilic substitution reaction leading to ring-opening of the epoxy and attachment of the DOPO, as discussed in detail elsewhere [27]. From the cone results of the GFRC of UP/PH-Ep:70/30 with and without FRs, the order of fire retardancy based on PHRR and THR is

$$\text{UP/PH-Ep:70/30-D} > \text{UP/PH-Ep:70/30-R} > \text{UP/PH-Ep:70/30} > \text{UP}$$

From Figure 1c and Table 2, it can be seen that the PHRR of UP/PH-Al:70/30-R is 368 (398 N) kW/m² (−17% w.r.t. that of UP and −10% w.r.t. that of UP/PH-Al:70/30), and the THR is 17.4 (18.8 N) MJ/m² (−38% compared to that of UP) with a char yield of 6%. The GFRC of UP/PH-Al:70/30-D composite has PHRR of 352 (306 N) kW/m² (−36% compared to that of UP) and THR of 24.2 (21.0 N) MJ/m² (−31% compared to that of UP) with a residue of 8% (refer Figure 3). The GFRC of UP/PH-Al:70/30-D samples show significant percentage reductions with respect to the UP and UP/PH-Al:70/30 composites for all cone parameters except for TSR (22% increase in TSR w.r.t. that of UP and 47% increase in TSR w.r.t. that of UP/PH-Al:70/30). From the above cone results, it is noted that both FRs act in the gas phase as well as in the condensed phase and effectively improve the fire retardancy of UP and UP/PH-Al composites. DOPO especially is more effective as a condensed phase FR in UP/PH-Al than is RDP (higher char yield in the former case). This may be because in co-cured UP/PH-Al blended composites, reaction of DOPO with a C=C bond of the allyl groups is responsible for the condensed phase action [27]. From the cone results for GFRC of UP/PH-Al with and without FRs, the order of fire retardancy based on the PHRR and THR is

$$\text{UP/PH-Al:70/30-D} > \text{UP/PH-Al:70/30-R} > \text{UP/PH-Al:70/30} > \text{UP}$$

The fire growth rate index, which is the ratio of the maximum value of the heat release rate (PHRR) and the time-to-PHRR, is an accepted method of evaluating the fire performance of materials. Higher FIGRA value means higher fire risk and faster flame spread [37]. FIGRA values for all samples are listed in the Table 2. The normalised FIGRA values of UP/PH-S:70/30-R and UP/PH-S:70/30-D are 5.4 and 4.8 kW/m²s, respectively, whereas UP composite has a FIGRA of 8.9 kW/m²s and UP/PH-S:70/30 a FIGRA of 5.5 kW/m²s. On the basis of the FIGRA values, DOPO is a more effective FR than RDP in GFRCs of UP/PH-S and UP/PH-Ep. The GFRCs of UP/PH-Al with RDP and DOPO show much lower FIGRA values of 5.5 and 3.9 kW/m²s, respectively, whereas the composite of UP/PH-Al:70/30 has a FIGRA of 6.7 kW/m²s. The lower FIGRA numbers indicate that the presence of FRs can improve the fire safety of the composite and hence reduce the fire risk. Based on the FIGRA values, the GFRC of the UP/PH-Al:70/30-D sample shows lowest fire risk of all the samples, which is the same as for the cast resins [27].

In Figure 4, a two-dimensional diagram of the overall fire safety performances evaluated from cone calorimetric results for GFRCs samples is presented. In Figure 4, THR (the total heat release) is plotted against fire growth rates calculated by dividing PHRR (peak heat release rate) by TTI (time-to-ignition). For materials to be fire safe, they should have low THR and PHRR/TTI values, i.e., data for these samples should fall close to the coordinates (0;0) on a two-dimensional (2-D) plot. All GFRCs of UP/PH with FRs fall within the region considered as having higher fire safety than UP and the UP/PH blends.

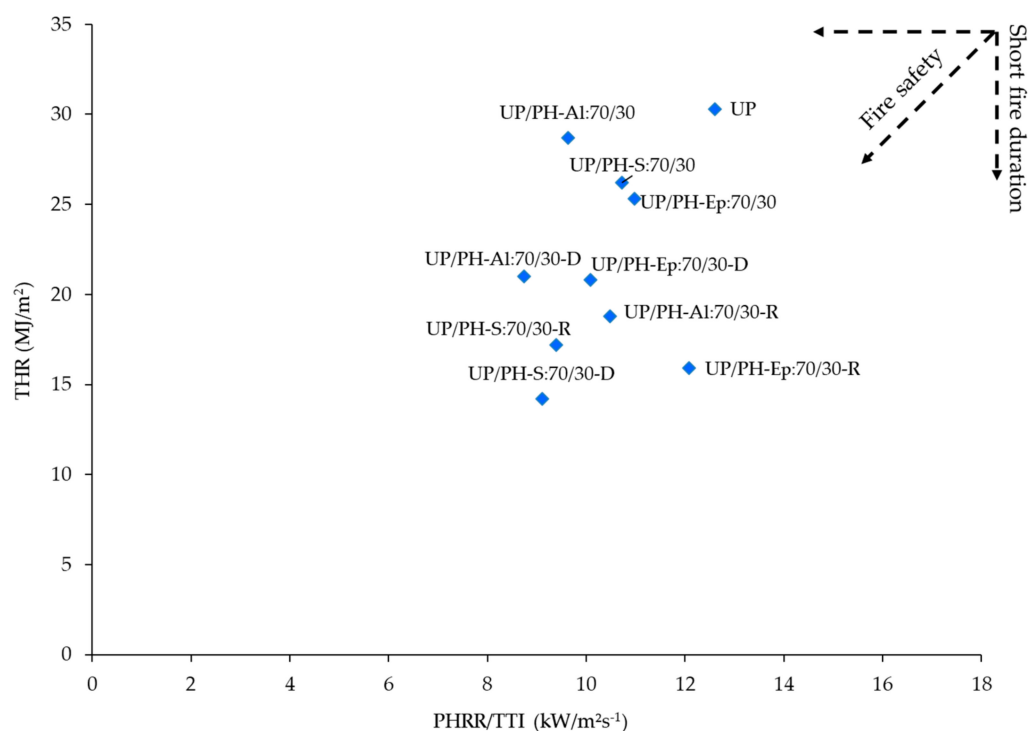


Figure 4. A fire safety assessment grid for GFRC of UP and its co-blended samples of UP/PH with and without FRs exposed to a 50 kW/m² heat flux.

3.1.2. UL-94 Results

The composite samples were tested under both vertical and horizontal UL-94 burning modes. In both tests, the samples were marked at 25 and 100 mm intervals from the exposed end, and from the time taken for the flame to travel from the first mark to the second (i.e., to travel 75 mm along the sample), burning rates could be calculated. UL-94 test results of GFRC of UP/PH:70/30 with FRs are listed in Table 3. All samples failed (completely burnt) in a vertical burning test except the UP/PH-Al:70/30-R composite sample, which gave a V-1 rating. From the tests, burnt lengths and times to burn were noted, from which rates of burning were calculated; these are listed in Table 3.

Table 3. UL-94 test results of GFRC samples of UP and of UP/PH co-blended matrices with FRs.

Samples	Horizontal Burning (HB) Rate (mm/min)	UL94 Rating for HB Test	Vertical Burning (VB) Rate (mm/min)	UL94 Rating for VB Test
UP	17.1 ± 0.1	HB	83.8 ± 2.3	FAIL
UP/PH-S:70/30	15.2 ± 0.7	HB	80 ± 1.7	FAIL
UP/PH-S:70/30-R	SE	HB	66 ± 1.2	FAIL
UP/PH-S:70/30-D	SE	HB	75 ± 1.5	FAIL
UP/PH-Ep:70/30	15.2 ± 0.3	HB	78.6 ± 2.0	FAIL
UP/PH-Ep:70/30-R	SE	HB	39 ± 1.6	FAIL
UP/PH-Ep:70/30-D	SE	HB	58.6 ± 1.9	FAIL
UP/PH-Al:70/30	13.6 ± 0.2	HB	57.2 ± 0.9	FAIL
UP/PH-Al:70/30-R	SE	HB	26.3 ± 1.1	V-1
UP/PH-Al:70/30-D	SE	HB	56.4 ± 1.2	FAIL

Note: SE—self-extinguish.

As can be seen in Table 3, the vertical burning rates of GFRC UP/PH-S:70/30-R and UP/PH-S:70/30-D are 66 mm/min and 75 mm/min, respectively, which are lower than those of UP (83.8 mm/min) and UP/PH-S:70/30 (80 mm/min) composites. However, the reduction in the rate of burning is much higher in the GFRCs of UP/PH-Ep and

UP/PH-Al samples with FRs present. This could be because in the GFRC of UP/PH-S blends, FRs acted only in the gas phase, i.e., the $\text{PO}\bullet$ radicals produced during thermal degradation trap $\text{H}\bullet$ and $\bullet\text{OH}$ radicals of the fire [27]. The vertical burning rates of UP/PH-Ep:70/30-R and UP/PH-Ep:70/30-D composites are 39 and 58.6 mm/min, respectively, which are much lower than UP (83.8 mm/min) as well as UP/PH-Ep:70/30 (78.6 mm/min) composite values. GFRCs of UP/PH-Al:70/30-R (26.3 mm/min) and UP/PH-Al:70/30-D (56.4 mm/min) show much lower burning rate than that of the UP composite. The vertical burning test results indicate that in the composites produced from the functionalised and compatibilised phenolic resin (PH-Al), the FRs are more active during combustion, probably acting both in condensed and gas phases. Of all the samples, the GFRC sample fabricated from UP/PH-Al:70/30-D gives the V-1 rating with the lowest burning rate of 26.3 mm/min.

In horizontal mode, the flame is applied to the free end of the horizontally mounted specimen for 30 s, and the HB rating is given to the sample if its burning rate is lower than 75 mm/min; this test was carried out on three samples. From Table 3 it can be seen that all the GFRC with FR samples self-extinguished after 30 s, which clearly shows that the presence of FRs reduces the propagation of flame in composites containing co-blended resin matrices.

3.2. Mechanical Performances of Fibre-Reinforced Composites with FRs

The mechanical performances of all GFRCs were evaluated in flexural, tensile and impact modes. Since the resin contents and, hence, fibre volume fractions (FVF) of these composites were different, selected mechanical properties (flexural and tensile moduli, E) have been normalised w.r.t. fibre volume fraction (FVF) using Equation (5), and the results are discussed in the following sections.

$$E_{\text{Normalised}} = \frac{E_{\text{Absolute}}}{FVF} \times 40 \quad (5)$$

3.2.1. Flexural Performance of UP and UP/PH Composites with FRs

Typical average stress vs. strain curves of selected samples are shown in Figure 5, and the calculated flexural moduli of all samples are given in Table 4. The flexural properties of GFRC of control samples such as UP and UP/PH blends have already been discussed in an earlier paper [29].

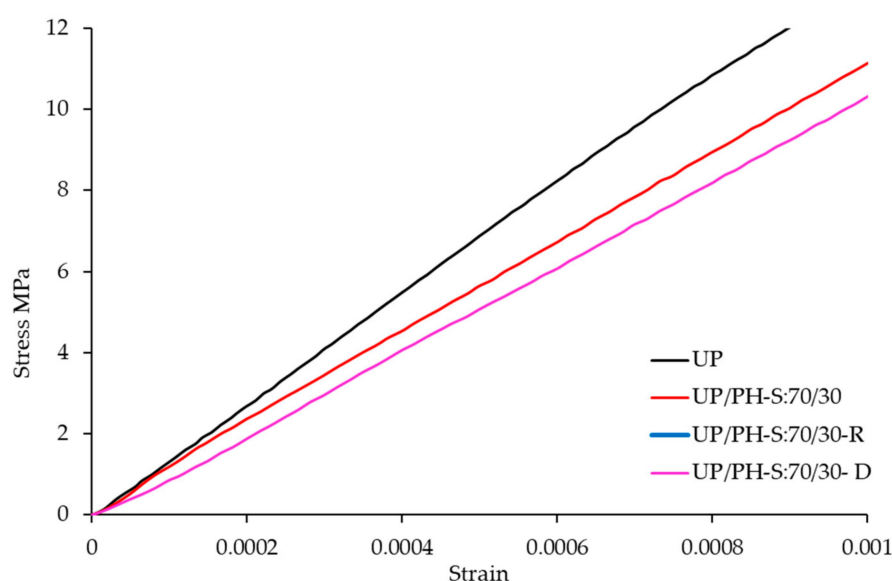


Figure 5. Stress vs. strain curves for GFRC of UP and UP/PH-S:70/30 with FRs under flexural mode.

Table 4. Mechanical properties of the GFRC from UP and UP/PH with FRs.

Sample	Initial Flexural Mod (GPa)		Tensile Properties		
	Absolute Value	Normalised to 40% FVF	Tensile Mod. (GPa)		Stress-at-Failure (MPa)
			Absolute Value	Normalised to 40% FVF	
UP	17.7 ± 0.6	18.0 ± 0.6	12.9 ± 0.8	13.2 ± 0.8	375 ± 13
UP/PH-S:70/30	10.9 ± 0.6	11.4 ± 0.5	11.6 ± 0.5	12.2 ± 0.5	281 ± 13
UP/PH-S:70/30-R	8.0 ± 0.7	9.4 ± 0.6	8.8 ± 0.7	10.4 ± 0.7	267 ± 2
UP/PH-S:70/30-D	9.6 ± 0.5	12.9 ± 0.7	10.9 ± 0.5	10.6 ± 0.6	242 ± 7
UP/PH-Ep:70/30	15.0 ± 0.6	15.7 ± 1.4	10.5 ± 1.0	11.2 ± 1.0	298 ± 6
UP/PH-Ep:70/30-R	8.6 ± 0.6	9.6 ± 0.9	9.6 ± 0.6	10.7 ± 0.8	216 ± 5
UP/PH-Ep:70/30-D	10.4 ± 0.9	9.3 ± 0.6	10.6 ± 0.9	9.4 ± 0.6	217 ± 8
UP/PH-Al:70/30	17.0 ± 0.6	17.8 ± 1.0	10.8 ± 0.3	12.0 ± 0.3	317 ± 8
UP/PH-Al:70/30-R	10.5 ± 0.7	11.1 ± 0.9	10.6 ± 0.7	11.1 ± 0.4	179 ± 7
UP/PH-Al:70/30-D	10.3 ± 0.6	16.8 ± 0.6	13.9 ± 0.6	12.1 ± 0.5	241 ± 6

It can be seen in Table 4 and Figure 2(a2) that the addition of RDP in 70/30 blended resin in UP/PH-S:70/30-R sample reduces the flexural modulus of the UP/PH-S:70/30 from 11.4 GPa to 9.4 GPa (48% reduction). The percentage reduction in flexural modulus of UP/PH-S:70/30-R w.r.t. that of UP (18 GPa) is 37%. RDP may have poor compatibility with UP and PH-S, affecting the cross-linking density, thus leading to a lower flexural modulus. In general, additives used in high concentrations lead to a reduction in mechanical performance of the polymer matrix [38,39]. DOPO, however, increases the modulus of the UP/PH-S:70/30 composite, indicating that it has a better compatibility.

The GFRCs of UP/PH-Ep:70/30-R and UP/PH-Ep:70/30-D samples show much lower flexural moduli of 9.6 GPa and 9.3 GPa, respectively, compared to the respective values for UP/PH-Ep:70/30 and UP composites. The behaviour of DOPO in sample UP/PH-Ep:70/30-D is surprising considering that DOPO should be chemically reactive with the epoxy functional group in the PH-Ep phenolic resin. The possible explanation of reduction could be that the incorporation of mono-functional fire retardant such as DOPO leads to a decrease in the cross-link density, as reactive epoxy groups in the PH-Ep phenolic resin are consumed to react with the fire retardant [40]. The reduced cross-link density would result in a decrease in flexural modulus [40].

The flexural modulus of UP/PH-Al:70/30-R is 11.1 GPa, and that of UP/PH-Al:70/30-D is 16.8 GPa. The presence of DOPO does not adversely affect the flexural properties of the UP/PH-Al blended composite (6% reduction w.r.t. that of UP/PH-Al:70/30 and 7% w.r.t. that of UP (Figure 2(c2))) when compared to results with RDP in UP/PH-Al:70/30-R (38% reduction w.r.t. that of UP/PH-Al:70/30 and 38% w.r.t. that of UP). This indicates RDP just acts as an additive-type FR with the UP/PH-Al:70/30 composite which has the flexural modulus 17.8 GPa. DOPO, on the other hand, appears to act as a reactive FR in UP/PH-Al blends, possibly by reaction of DOPO with the C=C bonds of the allyl groups as explained elsewhere [27].

3.2.2. Tensile Properties

Typical stress vs. strain curves for selected samples (UP/PH-Ep GFRC) under tensile mode are shown in Figure 6, and the analysed results for all the samples are given in Table 4. The tensile modulus of the GFRC of UP is 13.2 GPa, while for UP/PH-S:70/30-R, it is 10.4 GPa, and for UP/PH-S:70/30-D, it is 10.6 GPa. The tensile modulus of composites without FR (UP/PH-S:70/30) is 12.2 GPa. The reduction in tensile moduli for both FR types is similar, which is a different trend than for flexural modulus where RDP resulted in a greater reduction. The tensile properties of the composites though are fibre dominated, yet they also depend on other factors such as type and composition of matrix and adhesion between the matrix and the fibre. Hence, reduction in cross-linking of the blends also affects the tensile properties of the composites.

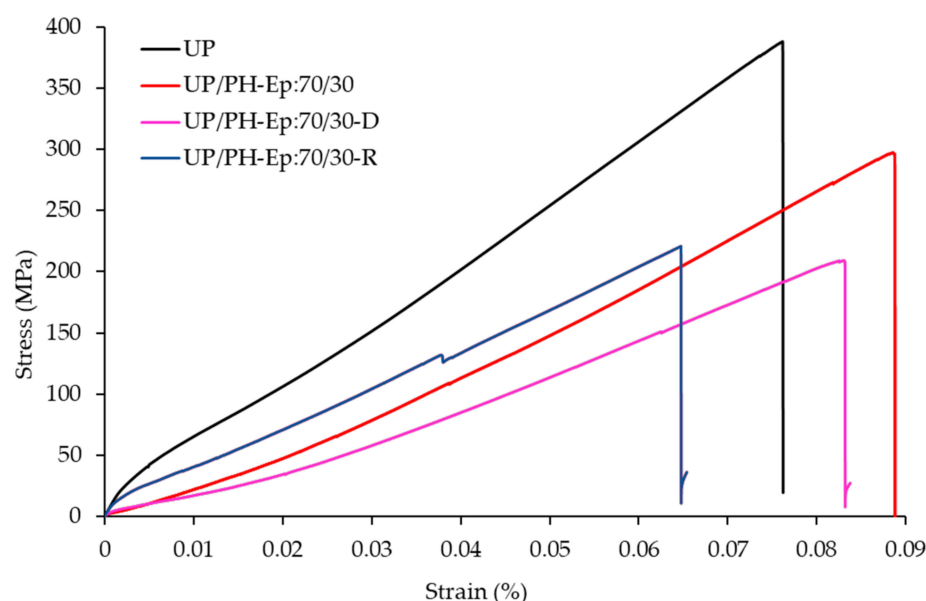


Figure 6. Stress vs. strain curves for GFRCs of UP and UP/PH-Ep:70/30 with FRs in tensile mode.

In Figures 4 and 6, it can be seen that the tensile moduli for samples of UP/PH-Ep composites containing RDP and DOPO are 10.7 GPa and 9.4 GPa, respectively, which are 19 and 29% less than the tensile modulus for the UP composite (Figure 2(b2)). These tensile moduli are also less than that of the UP/PH-Ep:70/30 composite. In the UP/PH-Ep blended resin system, the epoxy functional group acts as a linking group for the UP and PH-Ep resin and improves the compatibility between UP and PH-Ep. When RDP is added to UP/PH-Ep blends, the aromatic groups in RDP may react with methylol groups present in PH-Ep via the type of reaction involved in the curing of the PH-Ep [27]. However, when DOPO is added to UP and PH-Ep, the epoxy groups in PH-Ep react with the DOPO, causing ring-opening of the epoxy groups which become attached to the DOPO [27], and so reduce cross-linking between the UP and PH-Ep (acting as two phases). This indicates that the presence of FRs in UP/PH-Ep GFRC reduces the mechanical performance of the composites, as can clearly be seen from the data presented in Figure 2(b2) and Table 4.

The tensile modulus of the UP/PH-Al:70/30 GFRC is 12 GPa which is similar to that of the UP GFRC. This probably is because of the good compatibility between the UP and PH-Al, and so is one of the reasons why good mechanical properties are achieved also in GFRC of UP/PH-Al containing FRs. The GFRC of UP/PH-Al:70/30-D has a modulus of 12.1 GPa which is an 8% reduction with respect to that of the UP GFRC (Figure 2(c2)) and a 1% improvement with respect to that UP/PH-Al:70/30. As mentioned already, DOPO probably reacts with the UP/PH-Al through the C=C bonds of the allyl groups [27]. The samples with RDP also show only a 16% reduction w.r.t. in that UP and 8% with respect to that of UP/PH-Al:70/30.

The effect of the resin matrix can be seen in the stress-at-failure values, where the value decreased from that of the composite of UP (375 MPa) in the order UP/PH:70/30 (317–281 MPa) > UP/PH with FRs (267–179 MPa). Within the UP/PH samples, the most compatible blend, UP/PH-Al, has the highest stress-to-failure value and the least compatible, UP/PH-S, the lowest, indicating the effect of homogeneity of the cross-linked structure. The effect of each FR type on cross-linking of each blend can be seen in the reduction in stress-at-failure values of the respective samples.

Overall, the results show that there is not a significant impairment of tensile properties with the addition of FRs to the most compatible blended matrix system of UP/PH-Al with the significant improvement in the fire retardance. Among all the samples, UP/PH-Al:70/30-D has the best tensile and flexural properties.

3.2.3. Impact Properties

The impact test results in the form of load vs. deflection curves for all samples are shown in Figure 7a–c. After impact testing, the morphologies of the damaged areas on the tested samples were assessed using a digital camera. The images of the damaged samples of pre and post-fire impact test and the impact data are presented in Figure 8 and Table 5. As explained in Section 2.4, a 1J energy level was used as it caused some visible damage, but higher impact energy levels were not used in order to avoid excessive damage to the samples since these were subsequently to be tested for their fire performance and post-fire impact tolerance.

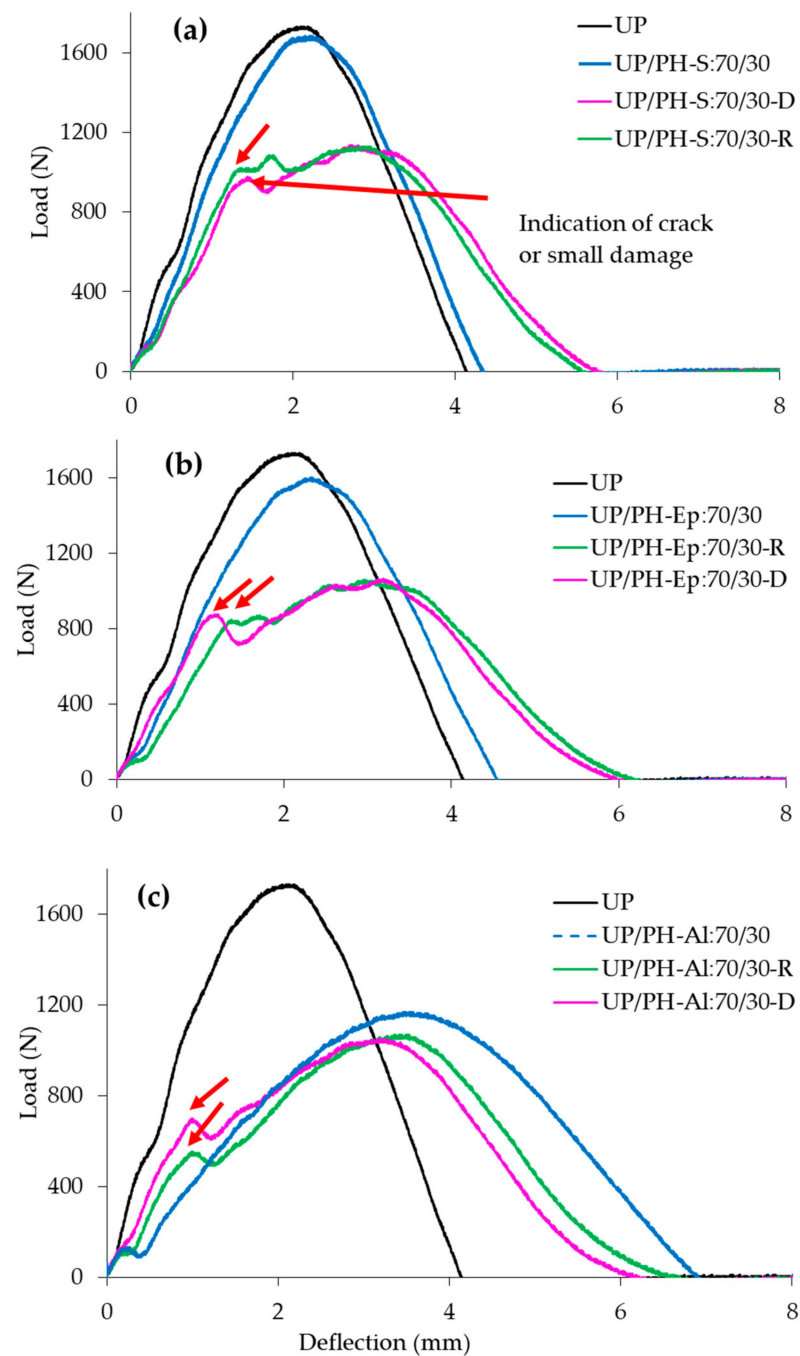
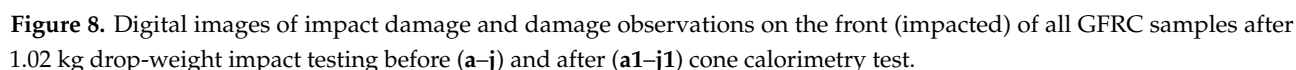


Figure 7. Load vs. deflection curves of GFRP of UP and (a) UP/PH-S, (b) UP/PH-Ep and (c) UP/PH-Al with FRs from drop-weight impact testing.



Sample ID	Before Burning		After Burning	
	Impact Modulus of Unburnt Samples (GPa)	% Change w.r.t. UP Value (%)	Impact Modulus of Cone Tested Samples (Gpa)	% Impact Modulus Retention (%)
UP	19.6 ± 0.6	0	0.35 ± 0.05	2
UP/PH-S:70/30	19.4 ± 0.6	−1	2.81 ± 0.02	14
UP/PH-S:70/30-R	13.9 ± 0.7	−29	-	-
UP/PH-S:70/30-D	20.1 ± 0.5	3	-	-
UP/PH-Ep:70/30	20.3 ± 0.5	4	2.51 ± 0.05	12
UP/PH-Ep:70/30-R	15.2 ± 0.6	−22	-	-
UP/PH-Ep:70/30-D	24.6 ± 0.9	26	3.17 ± 0.05	16
UP/PH-Al:70/30	19.7 ± 0.5	1	3.42 ± 0.05	17
UP/PH-Al:70/30-R	16.2 ± 0.7	−17	-	-
UP/PH-Al:70/30-D	25.8 ± 0.6	32	4.32 ± 0.05	21

In GFRC of UP sample, a visible impression of the tup of about 7.1 mm² area after impact testing can be seen; however, there is no physical damage, i.e., no delamination or fibre breakage. No damage is observed in the case of GFRC of UP/PH-S:70/30 sample.

Unlike UP/PH-S samples, the GFRC of UP/PH-S with FRs show a larger visible impression (damage or crack at the inner layers of the composites) on the GFRC surface by the impact tup than that of UP (see Figure 8), and the size of the impression is 132.7 mm^2 in GFRC of UP/PH-S:70/30-R and 63.8 mm^2 in UP/PH-S:70/30-D, respectively. From Figure 7a, the peak of the load vs. deflection curves of the GFRC with FRs is lower (maximum load tolerance is low) than that of GFRC of UP and UP/PH-S. The maximum load represents the peak load value that a composite laminate can tolerate, under a particular impact level before undergoing major damage [41]. However, the incorporation of FRs into the GFRC of UP/PH-S may lead to a potential increase in energy absorption with an indication of broader impact curves in Figure 7a. GFRC of UP/PH-S:70/30-R and UP/PH-S:70/30-D show the impact modulus of 13.9 GPa and 20.1 GPa, respectively, which is 20 and 4% reduction w.r.t. GFRC of UP/PH-S:70/30 and 29% reduction and 3% increase with respect to impact modulus of GFRC of UP. This indicates the FRs in the GFRC of UP/PH-S lead to more ductile behaviour and make the samples less brittle, possibly as a consequence of a plasticising effect of the FR.

From Figure 8, it can be seen that the damaged surface area of GFRC of UP/PH-Ep:70/30-R sample is 283.4 mm^2 and that of GFRC of UP/PH-Ep:70/30-D is 254.3 mm^2 whereas the GFRC of UP/PH-Ep:70/30 has surface damage of 113 mm^2 . This indicates that the maximum load tolerance is much reduced in GFRC with FRs. From Figure 7b, the shorter and broader load vs. deflection curves of UP/PH-Ep with FRs indicate that they can potentially absorb more impact energy than can GFRC of UP and UP/PH-Ep without FRs and also indicates the reduced brittleness and increased ductility.

From Figure 7c, the load vs. deflection curves of GFRC of UP/PH-Al with FRs show larger deflection, and the maximum load is shifted to higher deflections (see Figure 7c). This indicates that the time taken to cause maximum impact damage is longer than that of GFRC of UP and UP/PH-Al. We believe that the FRs may have a plasticising effect on the samples and because of this reduce the brittleness of the GFRC thus helping to prevent the onset of impact damage [41]. From Table 5, it can be seen that the GFRC of UP/PH-Al:70/30-R has a lower modulus (16.2 GPa) compared to that of GFRC of UP (19.6 GPa) and that the percentage reduction is 17% (Figure 2(c2)). In Figure 7c, the occurrence of a crack or other damage in GFRCs containing FRs can be easily identified from the inflections in the load vs. deflection curves. However, the GFRC of UP/PH-Al:70/30-D has an impact modulus of 25.8 GPa which is 32% higher than that of the UP composite and 31% higher than that of GFRC of UP/PH-Al:70/30. This further indicates the probable chemical reaction of UP/PH-Al blends with DOPO.

GFRC of UP/PH with added FRs show potential for good impact energy absorption by the FR presence. As already mentioned above, the FR may act as a plasticising agent and in so doing reduce the brittleness of the composites thus leading to higher deflection (Figure 7). UP/PH containing DOPO show higher impact modulus than that of UP/PH with RDP, possibly because of the reactive nature of the DOPO with the blended matrix. Impact damages indicate that the samples with added FRs have lower impact load tolerance than those of the GFRC without FRs.

3.2.4. Impact Test on Heat Damaged Composites

Impact tests were carried out on heat damaged GFRC samples of sizes $75 \text{ mm} \times 75 \text{ mm}$, after exposure in the cone calorimeter at 50 kW/m^2 external heat flux. The heat damaged samples of GFRC were tested under same impact testing conditions as control ones discussed in the above section. The impact test results for control, undamaged and heat damaged (cone tested) samples are given in Table 5. The GFRC of UP/PH-S shows better stiffness retention (% Modulus retention = Impact modulus of heat damaged sample $\times 100$ /Impact modulus of the respective control sample) than GFRC of UP and UP/PH-S with FRs. In Table 5, percentage retention values with respect to respective control samples are also given. GFRC of UP/PH-S:70/30 shows impact modulus value of 2.8 GPa. The cone exposed samples of GFRC of UP/PH-S with FRs had no mechanical integrity; the

steel impact tub pierced into the glass fibre layers of composites and created a hole in the sample, breaking the glass fibres as shown in Figure 8(e1,h1). This happened because of the lack of structural integrity and stiffness of the sample. The samples of UP/PH-Ep:70/30-R and UP/PH-Al:70/30-R show similar behaviour, i.e., no mechanical integrity of the sample. The deceleration modulus value could not be obtained for the samples with the holes. However, the DOPO containing UP/PH-S and UP/PH-Ep samples had better modulus retention than the respective control samples; the best results were shown by the GFRC sample of UP/PH-Al:70/30-D (21% retention).

4. Conclusions

This work has shown that the fire retardancy of GFRC of UP/PH-S, UP/PH-Ep and with UP/PH-Al can be further improved by the addition of RDP or DOPO. The fire-retardant action of these FR additives involves both gas-phase and condensed-phase actions in UP/PH-Ep and UP/PH-Al as established previously [27], and this is also supported by increased yields of both smoke and char on combustion in the present study. However, for GFRC of UP/PH-S, the FRs appear to be effective only in the gas-phase. The cone calorimetric results indicate that presence of RDP and DOPO reduced the PHRR by 30% and 30% and THR by 43% and 53%, respectively; however, the reductions were less than those seen in the respective cast resin samples, reported previously [27]. In GFRC samples, the glass fibres entrap/delay the release of some volatiles produced during burning of the resin and act as a thermal insulator. The GFRC of UP/PH-Al with DOPO showed highest fire retardancy (PHRR reduced by 36% and THR by 31%) compared with those of the UP composite and the GFRC samples of UP/PH-S and UP/PH-Ep. In UL-94 tests, while all composites except UP/PH-Al:70/30-R failed the test, in horizontal tests, all self-extinguished, indicating that these composites will show good performance when tested for surface flame spread. The effects of fire retardants on mechanical properties depended on the type of test. While RDP reduced the flexural (by 13–48%), DOPO had a little effect (by 1–7% in UP/PH-S and UP/PH-Al, but by 38% in UP/PH-Ep). Neither FR had an effect on impact moduli of UP/PH-S composites, but both reduced those of UP/PH-Ep by 17–22% and increased those of UP/PH-Al by 26–32%. Both fire retardants had little effect on the tensile modulus of UP/PH-S:70/30 but decreased it in the more compatible UP/PH-Ep:70/30 and UP/PH-Al:70/30 systems, which may be a consequence of the fire retardants acting as plasticisers in these systems and affecting the fibre–matrix adhesion. Amongst the different samples, the sample from GFRC of UP/PH-Al with DOPO shows the best fire retardancy with a normalised PHRR of 306 kW/m² which is 36% lower than that of UP and with only a small adverse effect of the DOPO on mechanical performance (the tensile modulus of UP/PH-Al with DOPO is 12.1 GPa and for UP it is 13.8 GPa).

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